Vibrational spectroscopy of the borate mineral tunellite $SrB_6O_9(OH)_2 \cdot 3(H_2O)$ – implications for the molecular structure

Ray L. Frost[1•] , Andrés López[1], Ricardo Scholz [2] and Yunfei Xi [1]

[1.] School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane Queensland 4001, Australia.

[2.] Geology Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG, 35,400-00, Brazil

Abstract:

Tunellite is a strontium borate mineral with formula: $SrB_6O_9(OH)_2 \cdot 3(H_2O)$ and occurs as colorless crystals in the monoclinic pyramidal crystal system. An intense Raman band at 994 cm^{-1} was assigned to the BO stretching vibration of the B_2O_3 units. Raman bands at 1043, 1063, 1082 and 1113 cm^{-1} are attributed to the in-plane bending vibrations of trigonal boron. Sharp Raman bands observed at 464, 480, 523, 568 and 639 cm^{-1} are simply defined as trigonal and tetrahedral borate bending modes. The Raman spectrum clearly shows intense Raman bands at 3567 and 3614 cm^{-1}, attributed to OH units. The molecular structure of a natural tunellite has been assessed by using vibrational spectroscopy.

Key words: Raman spectroscopy, borate, tunellite, infrared, evaporite

• Author to whom correspondence should be addressed (r.frost@qut.edu.au)

Introduction

The mineral tunellite [1, 2] is hydrated hydroxy borate of strontium of formula $SrB_6O_9(OH)_2 \cdot 3H_2O$. The mineral is a rare mineral formed in borate deposits. The mineral is named after George Gerard Tunell, Jr. (1900–1996), Professor of Geology, University of California, Los Angeles, California, USA. The mineral is known from a significant number of deposits worldwide [1, 3-6].

Tunellite is one member of a series of borate compounds of the borate series $M^{2+}O.3B_2O_3 \cdot xH_2O$ [7]. Other borate minerals include veatchite (Sr), p-veatchite (Sr) with x=2, nobleite (Ca), with x=4, aksaite (Mg) and gowerite (Ca) with x=5 [7]. Many synthetic borates with this fundamental formula have been forthcoming. The chemistry of tunellite including its thermal decomposition has been studied by Gulensoy and Teberdar [8]. The effect of heat treatment on the structural properties of the tunellite has been studied [9]. Hydrogen bonding in tunellite has been elucidated [10]. Boron NMR spectroscopy has proven useful for the study of the polyanions in tunellite [11].

Tunellite is monoclinic with point group 2/*m* [2, 7]. The cell characteristics are *P*21/*a with a* = 14.415(3), *b* = 8.213(1), *c* = 9.951(2), β= 114.05(1)_ and *Z* = 4. Tunellite occurs in prismatic crystals up to 10 cm long or compact fine-grained nodules. The crystal structure contains infinite sheets composed of polymerized borate polyanions, with Sr2+ cations and water molecules filling available spaces in and near the sheets [7]. Adjacent sheets are held together solely by bonds to water molecules [7]. The polymerized borate polyanions are composed of individual borate groups, each group containing three B-O tetrahedra and three B-O triangles.

Vibrational spectroscopy has been applied to borate glasses [12-15]. There have been a number of studies of borate glasses doped with a wide range of radioactive atoms [16, 17]. Borate glasses are used as a means of containment of radioactive materials. There have been a number of studies looking at the effect of radiation on borate glasses [18, 19]. If there is to be an understanding of borate glasses and their role in radioactive element containment, then an understanding of the vibrational spectroscopy of borate minerals needs to be undertaken. The number of vibrational spectroscopic studies of borate minerals is quite few and far between [20-23]. The number of Raman studies of borate minerals is also very limited [24, 25]. There have been a number of infrared studies of some natural borates [26-29]. Most of

these references are not new and there have been no recent studies on the vibrational spectroscopy of natural borates. Ross in Farmer's treatise reported the infrared spectra of several borate minerals [30].

The use of infrared spectroscopy is limited by the spatial resolution of the technique which is around 25 microns. In comparison, the spatial resolution using Raman spectroscopy is 1 micron. Thus, when studying a mineral using spectroscopic techniques it is advantageous to use Raman spectroscopy. The selection of the target mineral is more easily made. With infrared spectroscopy, any impurities will be measured as well as the target mineral. Raman spectroscopy has proven most useful for the study of secondary minerals [25, 31-36].

To the best of the authors' knowledge, there have been very few infrared spectroscopic studies of tunellite type structure [29, 37] and no Raman studies of this natural mineral have been forthcoming. The objective of this paper is to report the vibrational spectroscopic study of a natural tunellite mineral and relate the spectra to the molecular chemistry and the crystal chemistry of this borate mineral. We have characterised tunellite using a combination of Raman and infrared spectroscopy.

Experimental

Mineral

Samples description and preparation

The tunellite sample studied in this work forms part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAC-103. Details of the mineral have been published (page 80, Vol. 5) [38]. The sample originated from US Borax mine, Kramer district, Boron, California, USA.

The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. Scanning electron microscopy (SEM) in the EDS mode was applied to support the mineral characterization.

The SEM image and the chemical analysis is given in the supplementary information.

Raman spectroscopy

Crystals of tunellite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10x, 20x, and 50x objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He-Ne laser producing highly polarised light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of ± 1 cm^{-1} in the range between 200 and 4000 cm^{-1}. Repeated acquisitions on the crystals using the highest magnification (50x) were accumulated to improve the signal to noise ratio of the spectra. The spectra were collected over night. Raman Spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer. The Raman spectrum of at least 10 crystals was collected to ensure the consistency of the spectra.

Infrared spectroscopy

Infrared spectra were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of 128 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio. The infrared spectra are given in the supplementary information.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian-Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Lorentzian-Gaussian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Results and Discussion

The Raman spectrum of tunellite in the 4000 to 100 cm^{-1} region is displayed in Figure 1a. This figure reports the position of the Raman bands and their relative intensity. It is noted that there are parts of the spectrum where no intensity is observed. Therefore, the spectrum is subdivided into sections in subsequent figures so that more detailed assessment of the spectrum can be made. In a similar way, the infrared spectrum of tunellite in the 4000 to 500 cm^{-1} region is reported in Figure 1b. The spectrum is not shown below 500 cm^{-1}. The reason for this is that we are using a reflectance technique and the ATR cell absorbs all incident radiation. In a similar fashion to the Raman spectrum, the infrared spectrum is divided into sections depending upon the types of vibrations being observed.

The Raman spectrum of tunellite in the 1200 to 700 cm^{-1} spectral range is reported in Figure 2a. The infrared spectrum of tunellite in the 1200 to 700 cm^{-1} spectral range is reported in Figure 2b. The Raman spectrum in this spectral region is dominated by a sharp intense band at 994 cm^{-1}. Bands of significantly lesser intensity are observed at 1043, 1063, 1082 and 1113 cm^{-1}. The Raman band at 994 cm^{-1} is assigned to the BO stretching vibration of the B_6O_9 units. The Raman bands at 1043, 1063, 1082 and 1113 cm^{-1} are attributed to the BOH in-plane bending modes. Iliev *et al.* determined the Raman spectrum of a synthetic cobalt tunellite [39]. The symmetry species of some vibrational modes were determined. Iliev *et al.* [40] used Raman imaging to show the ferroelectric properties of tunellite type compounds. These workers [40] showed that tunellites exhibit a sequence of transitions from the high temperature paraelectric cubic phase to ferroelectric orthorhombic, monoclinic, trigonal phases, and finally to a monoclinic phase at low temperatures where both ferroelectric and magnetic orders coexist. Kim and Somoano determined the improper ferroelectric transition using Raman spectroscopy [41].

In contrast, the infrared spectrum of tunellite (Figure 2b) shows complexity with many overlapping bands, making the assignment of the infrared bands very difficult. The intense infrared band at 960 cm^{-1} with shoulders at 929, 947 and 985 cm^{-1} is assigned to the trigonal borate stretching modes. The overlapping infrared bands at 784, 809, 844, 863 and 877 cm^{-1} are attributed to the infrared tetrahedral borate stretching and bending vibrations. The series of bands from 669 through to 737 cm^{-1} are related to trigonal borate bending modes.

The Raman spectra in the 700 to 400 cm^{-1} and in the 300 to 100 cm^{-1} spectral range are illustrated in Figures 3a and 3b. Sharp Raman bands are observed at 464, 480, 523, 568 and 639 cm^{-1}. These bands are simply defined as trigonal and tetrahedral borate bending modes. A series of infrared bands at 669, 679, 699, 708, 728 and 737 cm^{-1} (Figure 4b) are due to these bending modes. Strong Raman bands are found in the far wavenumber region at 150, 332 and 371 cm^{-1} (Figure 3b). These bands may be simply described as lattice vibrations.

Raman spectrum of tunellite in the 3800 to 2700 cm^{-1} spectral range and the infrared spectrum of tunellite in the 3700 to 2500 cm^{-1} spectral range are reported in Figures 4a and 4b. According to the commonly accepted formula of tunellite $SrB_6O_9(OH)_2{\cdot}3(H_2O)$, both water or OH groups are found in the formula of the mineral. The Raman spectrum clearly shows intense Raman bands at 3567 and 3614 cm^{-1}. These bands are assigned to the stretching vibrations of the OH units. Two OH-stretching bands in the Raman spectra of the mineral, at 3405 and 3494 cm^{-1}, respectively, are indicative of two distinct hydrogen positions in the structure. Other strong intensity bands at 3243, 3282, 3324, 3369, 3383 and 3430 cm^{-1} are found. These broader bands are assigned to water stretching vibrations.
The infrared spectrum in the 1800 to 1300 cm^{-1} region is reported in Figure 5. An infrared band centred upon 1677 cm^{-1} is observed which may be band component analysed into several components at 1631, 1660 and 1727 cm^{-1}. These bands are attributed to water bending vibrations. The intensity as observed in the infrared spectrum is quite strong with a broad band at 1631 cm^{-1} found.

The development of these type of compounds such as tunellite rests with their ferromagnetic and pyro-electric properties [42]. The development of piezoelectric properties is time continuous [43, 44]. Also a hydroxy compound has been synthesised [45], although the vibrational spectroscopy of this compound was not reported. In the infrared spectrum (Figure 4b) a series of low intensity bands are observed.

Conclusions

There are many borate minerals which have yet to have their vibrational spectrum determined and the molecular structure assessed in terms of their vibrational spectrum. In this work we have measured the Raman and infrared spectrum of tunellite, a hydrated hydroxy borate mineral of calcium with formula: $SrB_6O_9(OH)_2{\cdot}3(H_2O)$. The importance of the mineral

tunellite rests with the chemistry of the compound and the range of isomorphic substitutions which can be made in order to produce specially selected ferroelectric, pyroelectric and piezoelectric properties.

The Raman spectrum in this spectral region is dominated by a sharp intense band at 994 cm^{-1}. Bands of significantly lesser intensity are observed at 1043, 1063, 1082 and 1113 cm^{-1}. The Raman band at 994 cm^{-1} is assigned to the BO stretching vibration of the B_6O_9 units.

Acknowledgments

The financial and infra-structure support of the School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, is gratefully acknowledged. The Australian Research Council (ARC) is thanked for funding the instrumentation. R. Scholz thanks to FAPEMIG – Fundação de Amparo à Pesquisa do estado de Minas Gerais, (grant No. CRA - APQ-03998-10).

References

[1] R.C. Erd, V. Morgan, J.R. Clark, U.S. Geological Survey Professional Paper No. 424-C (1961) 294.

[2] H. Gulensoy, T. Teberdar, Bull. Min. Res. Explor. Instit. Turk. No. 79 (1972) 30.

[3] O. Baysal, Bull. Min. Res. Explor. Instit. Turk. No. 79 (1972) 22.

[4] W. Berdesinski, H. Meixner, Neues Jahrb. Min.104 (1965) 93.

[5] C. Helvaci, Min. Dep. 19 (1984) 217.

[6] C. Helvaci, R.N. Alonso, Turk.J.Earth Sc. 9 (2000) 1.

[7] J.R. Clark, Amer. Min. 49 (1964) 1548.

[8] H. Gulensoy, T. Teberdar, Bull. Min. Res. Explor. Instit. Turk. No. 79 (1972) 50.

[9] M.S. Yilmaz, S. Piskin, J. Chem. Soc. Pak. 34 (2012) 526.

[10] P.C. Burns, F.C. Hawthorne, Can. Min. 32 (1994) 895.

[11] J.D. Cuthbert, W.T. MacFarlane, H.E. Petch, J. Chem. Phys. 43 (1965) 173.

[12] I. Ardelean, S. Cora, J. Mat. Sc.19 (2008) 584.

[13] I. Ardelean, S. Cora, J. Optoelect. Adv. Mat. 12 (2010) 239.

[14] I. Ardelean, L. Griguta, J. Optoelect. Adv. Mat. 9 (2007) 2068.

[15] I. Ardelean, V. Timar, J. Optoelect. Adv. Mat. 10 (2008) 246.

[16] F.H. El Batal, M.A. Azooz, A.A. El-Kheshen, Trans. Ind. Cer. Soc. 68 (2009) 81.

[17] F.H. ElBatal, Y.M. Hamdy, Trans. Ind. Cer. Soc. 67 (2008) 193.

[18] C. Rajyasree, P.M. Vinaya Teja, K.V.R. Murthy, D. Krishna Rao, Physica B406 (2011) 4366.

[19] B. Sumalatha, I. Omkaram, T.R. Rao, C.L. Raju, J. Non-Cryst. Solids 357 (2011) 3143.

[20] M. Mir, J. Janczak, Y.P. Mascarenhas, J. App. Cryst. 39 (2006) 42.

[21] I. Mitov, Z. Cherkezova-Zheleva, V. Mitrov, J. Balkan Trib. Ass. 4 (1998) 191.

[22] A.S. Povarennykh, E.I. Nefedov, Geol. Zh. (Russian Edition) 31 (1971) 13.

[23] V.S. Suknev, E.N. Diman, Zh. Prikladnoi Spek. 10 (1969) 326.

[24] V.F. Ross, J.O. Edwards, Chem. Boron Its Compd. (1967) 15.

[25] R.L. Frost, J. Raman Spectrosc. 42 (2011) 540.

[26] M.V. Akhmanova, Zh. Struk. Khim. 3 (1962) 28.

[27] D.A. Long, R.T. Bailey, Spectrochim. Acta A19 (1963) 1607.

[28] A. Vasko, I. Srb, Czech. J. Phys. 17 (1967) 1110.

[29] C.E. Weir, J. Res. Nat. Bur. Stand. A70 (1966) 153.

[30] V.C. Farmer, Mineralogical Society Monograph 4: The Infrared Spectra of Minerals. London, 1974.

[31] R.L. Frost, S. Bahfenne, J. Raman Spectrosc. 42 (2011) 219.

[32] R.L. Frost, S. Bahfenne, J. Cejka, J. Sejkora, J. Plasil, S.J. Palmer, E.C. Keeffe, I. Nemec, J. Raman Spectrosc. 42 (2011) 56.

[33] R.L. Frost, J. Cejka, J. Sejkora, J. Plasil, B.J. Reddy, E.C. Keeffe, Spectrochim. Acta, A78 (2011) 494.

[34] R.L. Frost, S.J. Palmer, Spectrochim. Acta, A78 (2011) 1250.

[35] R.L. Frost, S.J. Palmer, H.J. Spratt, W.N. Martens, J. Mol. Struct. 988 (2011) 52.

[36] R.L. Frost, J. Sejkora, J. Cejka, J. Plasil, S. Bahfenne, E.C. Keeffe, J. Raman Spectrosc. 42 (2011) 534.

[37] C. Helvaci, Mercian Geol. 6 (1978) 257.

[38] J.W. Anthony, R.A. bideaux, K.W. Bladh, M.C. Nichols, Silica, Silicates. Mineral data Publishing, Tucson, Arizona, 1995.

[39] M.N. Iliev, V.G. Hadjiev, M.E. Mendoza, J. Pascual, Phys. Rev. B76 (2007) 214112/1.

[40] M.N. Iliev, V.G. Hadjiev, J. Iniguez, J. Pascual, Acta Phys. Polonica, A116 (2009) 19.

[41] Q. Kim, R.B. Somoano, Ferroelectrics 36 (1981) 431.

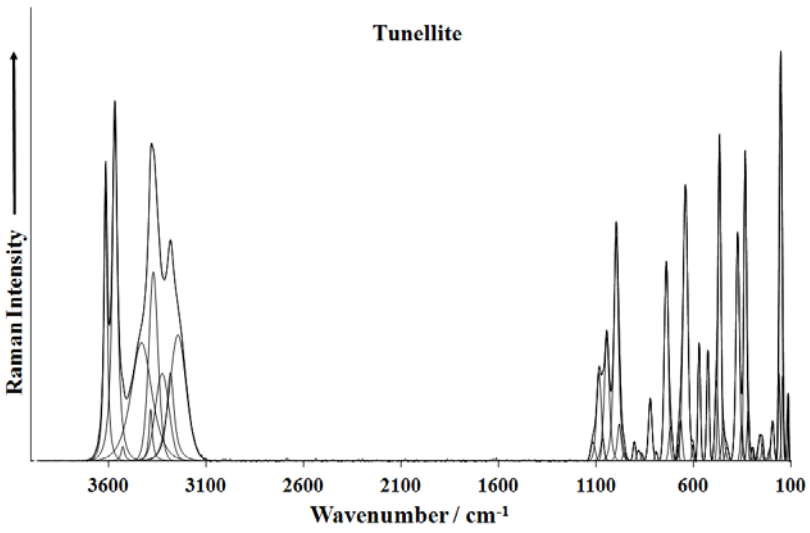
[42] A.G. Castellanos-Guzman, ISAF '94, Proceedings of the IEEE International Symposium on Applications of Ferroelectrics, 9th, University Park, Pa., Aug. 7-10, 1994 (1994) 6.

[43] O. Crottaz, J.P. Rivera, H. Schmid, J. Korean Phys. Soc. 32 (1998) S1261.

[44] M. Delfino, G.M. Loiacono, P.S. Gentile, Inorgan. Chim. Acta 43 (1980) 59.

[45] U. Werthmann, H. Gies, J. Glinnemann, T. Hahn, Zeit. Krist. 215 (2000) 393.

List of Figures



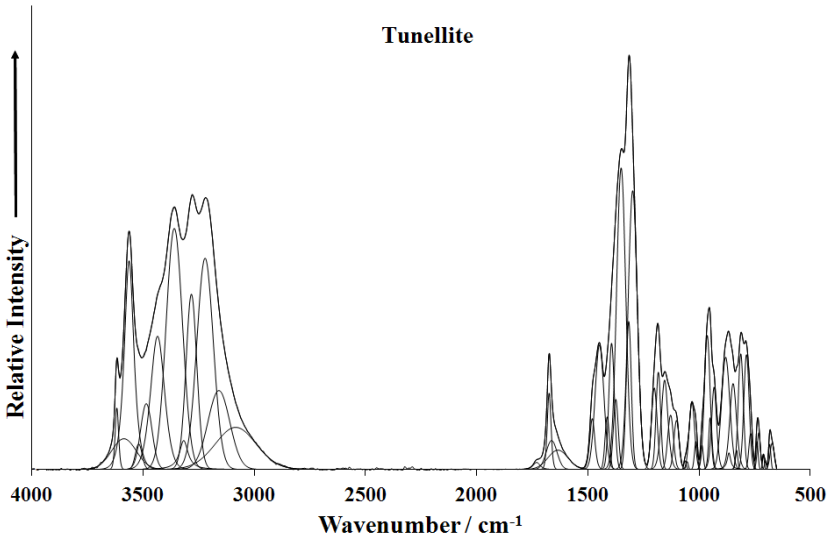
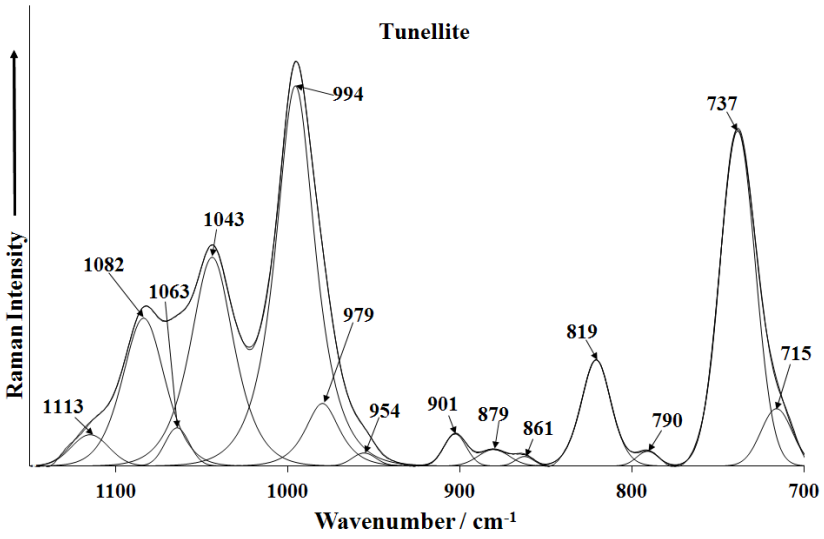


Figure 1a Raman spectrum of tunellite (upper spectrum) over the 4000 to 100 cm^{-1} spectral range and Figure 1b infrared spectrum of tunellite (lower spectrum) over the 4000 to 500 cm^{-1} spectral range



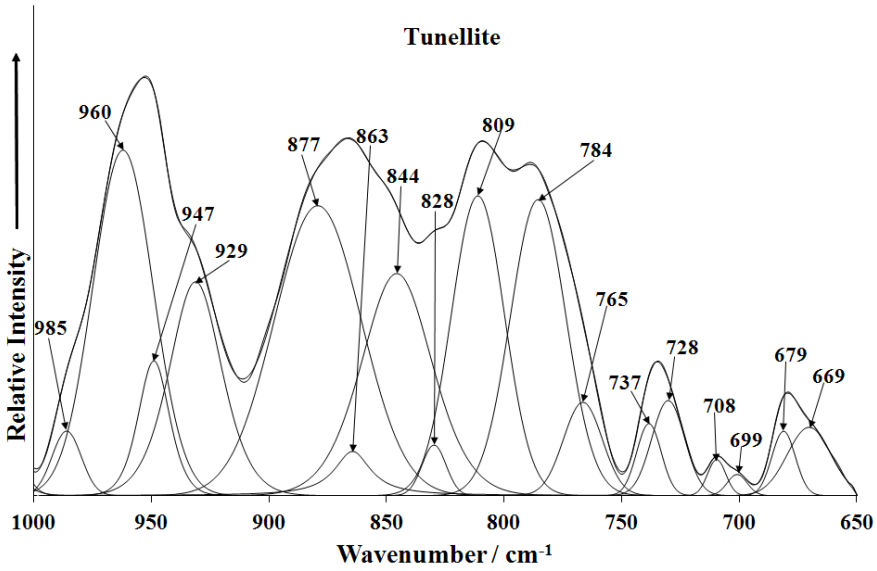
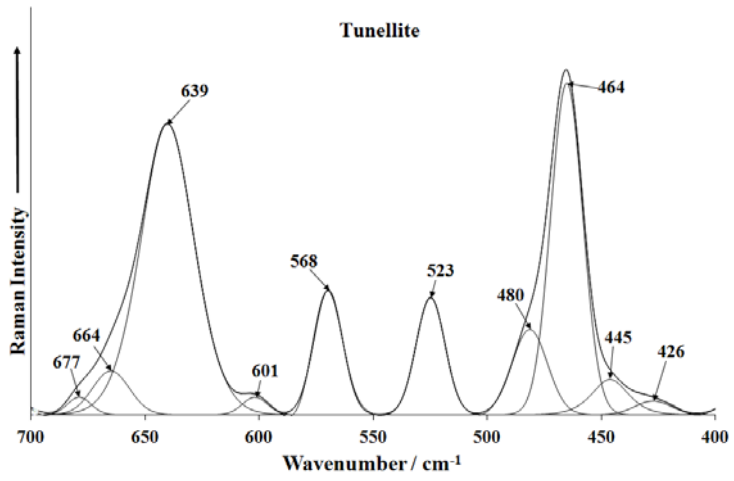


Figure 2 (a) Raman spectrum of tunellite over the 1200 to 700 cm^{-1} spectral range (b) Infrared spectrum of tunellite over the 1000 to 650 cm^{-1} spectral range



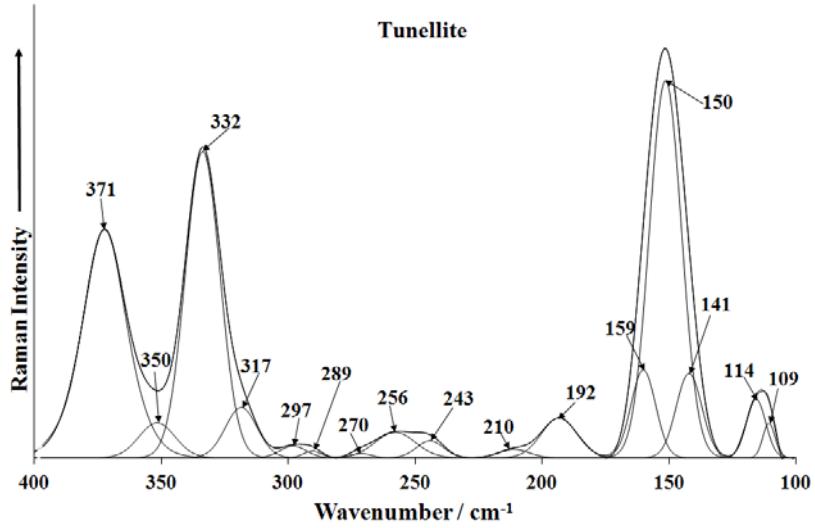
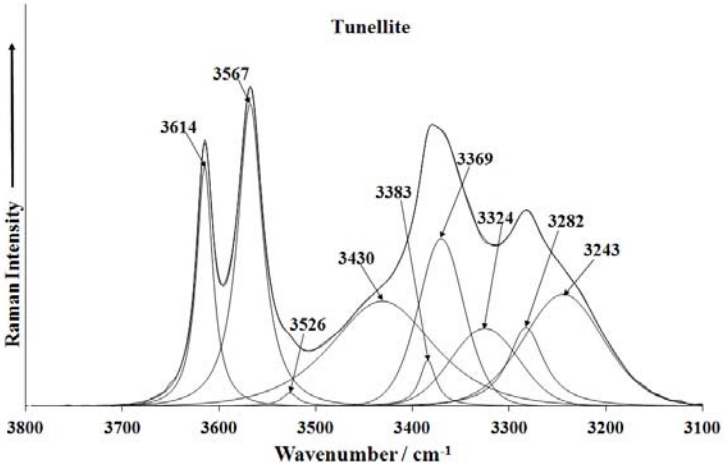


Figure3 Raman spectrum of tunellite (upper spectrum) in the 700 to 400 cm^{-1} spectral range and Figure 3b infrared spectrum of tunellite (lower spectrum) in the 400 to 100 cm^{-1} spectral range



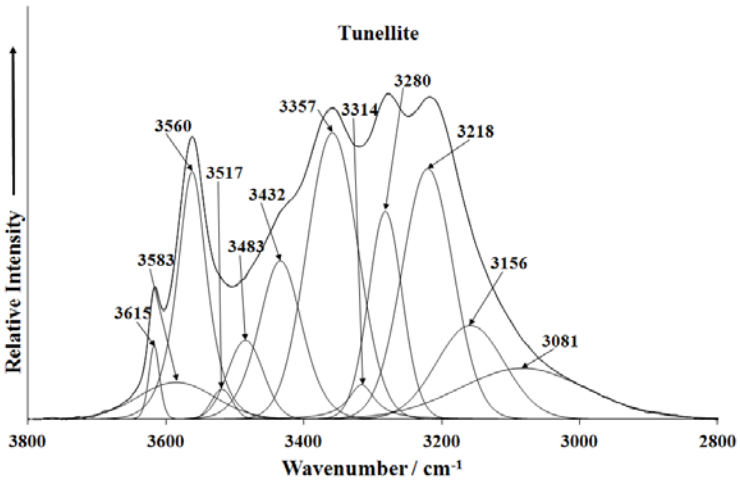


Figure 4a Raman spectrum of tunellite (upper spectrum) in the 3800 to 3100 cm^{-1} spectral range and Figure 4b Infrared spectrum of tunellite (lower spectrum) in the 3800 to 2800 cm^{-1} spectral range

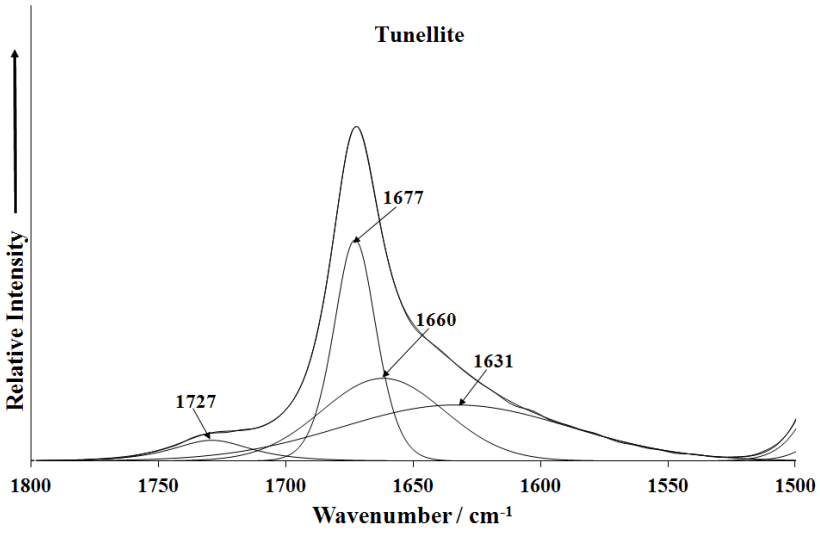


Figure 5 Infrared spectrum of tunellite over the 1800 to 1500 cm^{-1} spectral range